- Field assessment of vinasse application in sugarcane fields
- Vinasse transport was assessed in vadose zone and aquifer
- Major ions were efficiently retained due to vadose zone processes and plant uptake

*graphical abstract



# Vinasse application to sugar cane fields. Effect on the unsaturated zone and groundwater at Valle del Cauca (Colombia)

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## Abstract

Extensive application of vinasse, a subproduct from sugar cane plantations for bioethanol production, is currently taking place as a source of nutrients that forms part of agricultural management in different agroclimatic regions. Liquid vinasse composition is characterised by high variability of organic compounds and major ions, acid pH (4.7), high TDS concentration (117,416-599,400 mg $L^{-1}$) and elevated EC (14,350-64,099 µS $cm^{-1}$). A large-scale sugar cane field application is taking place in Valle del Cauca (Colombia), where monitoring of soil, unsaturated zone and the aquifer underneath has been made since 2006 to evaluate possible impacts on three experimental plots. For this assessment, monitoring wells and piezometers were installed to determine groundwater flow and water samples were collected for chemical analysis. In the unsaturated zone, tensiometers were installed at different depths to determine flow patterns, while suction lysimeters were used for water samples chemical determinations. The findings show that in the sandy loam plot (Hacienda Real), the unsaturated zone is characterised by low water retention, showing a high transport capacity, while the other two plots of silty composition presented temporal saturation due to La Niña event (2010-2011). The strong La Niña effect on aquifer recharge which would dilute the infiltrated water during the monitoring period and, on the other hand dissolution of possible precipitated salts bringing them back into solution may occur. A slight increase in the concentration of major ions was observed in groundwater (~5% of TDS), which can be attributed to a combination of factors: vinasse dilution produced by water input and hydrochemical processes along with nutrients removal produced by sugar cane uptake. This fact may make the aquifer vulnerable to contamination.

**Keywords**: monitoring, unsaturated zone, environmental impact, stillage, vinasse.

## 1. Introduction

Sugar cane is an extensively grown grass crop in tropical and subtropical areas worldwide. It is produced predominantly for juice, extracted for sucrose, but can be also used for fermentation products, such as ethanol and acetic acid. Ethanol is a fuel produced from renewable sources with low carbon levels. These two characteristics confer ethanol strategic importance to fight against the intensification of greenhouse effects and their influence on global climate change, which falls in line with sustainable development principles. In 2001, the National Act (Law 693, of 19 September 2001) to enhance production and use of sugar cane alcohol distillation (ethanol), was incorporated into the legal framework of Colombia. One of the principal objectives of the National Act was to provide the legal provision for implementing a more efficient enviro-friendly use of motor engine fuel by substituting a certain amount of petrol-derived substances (around 10%) for biofuel to reduce atmospheric pollution.

The Colombian Fuel Oxygenation Policy increases bioethanol production in the sugar cane refineries in South-western Colombia and consequently led to growing vinasse production. Vinasse (stillage) is a residual subproduct of the ethanol industrial process, currently used as a solid/liquid fertiliser and a soil conditioner in sugar cane fields. In general, each litre of ethanol generates between 1-14 litres of vinasse (CVC, 2012a). Liquid vinasse is light brown in colour. It has low total solids content, from 2-4% when obtained from straight sugar cane juice and 5-10% when obtained from sugar cane molasses. Its turbidity is high, composed with high variable composition mainly of organic compounds (acids, alcohols, aldehydes, ketones, esters and sugars) and ions ($K^+$, $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$). It has a low pH (~5) and a high Chemical Oxigen Demand-QOD (Table 1).

Large-scale vinasse applications are an effective economic alternative for sugar cane irrigation and fertilisation given their high levels of potassium, calcium and organic matter in the chemical composition, as well as moderate amounts of nitrogen and other nutrients (Prado et al., 2013). However, such applications have been reported to confer both benefits and demerits for soil quality, water and sugar cane production in field trial research, and in different agroclimatic regions (Da Silva et al., 2007; Prado et al., 2013; Teixeira et al., 2010).

Limited information about the possible impacts of vinasse application on soil and water media at experimental sites has been found, and very few experimental research projects have been undertaken to date (Christofoletti et al., 2013; Gloeden et al., 1991). Research studies have focused mainly on flora and fauna vinasse toxicity (Da Silva et al., 2007). Results from lysimeter studies have indicated that vinasse does not negatively affect soil pH and salinity, and it slightly increases soil organic carbon and exchangeable $K^+$ in Mauritius soils (Soobadar and Ng Kee Kwong, 2012). Nitrate flux increase has also been observed in the laboratory experiments by Eykelbosh et al. (2015). Moreover, addition of sugar cane vinasse to soil has been reported to influence the persistence and sorption of herbicides diuron, hexazinone and tebuthiuron in clay and sandy soils of Brazil (Lourencetti et al., 2012), and also nitrogen leaching in the Botucatu aquifer recharge area (Gloeden et al., 1991). Elevated Dissolved Organic Carbon-DOC in groundwater beneath irrigated sugar cane under sugarcane by-products application has been found in tropical Australia (Thavalakumaran et al., 2014). A drop in soil bulk density and increased porosity (Jiang et al., 2012) after a 3-year application in an experimental sugar field location of Guanxi (PR China) have been observed, while negative effects on soil permeability through vinasse application from processing beet have been reported by Tejada et al. (2006). Change of mineralogical properties of soils after more than 40 years of irrigation has been found by Rosabal et al. (2007) in Cuban soils. In laboratory experiments, Miyamoto et al. (2012) indicated a decrease in saturated and unsaturated hydraulic conductivity by physical clogging and nitrate leaching (Eykelbosh et al., 2015) after sugar cane vinasse applications. A high contamination potential of surface waters, which caused water temperature and acidification to rise, and turbidity and oxygen depletion to increase, has been observed in the Ipojuca River (Brazil) by Gunkel et al. (2007). A change in the physico-chemical characteristics of groundwater after intensive fertigation with vinasse has been noted in sandy soils and temperate climate by Hassuda (1989), Ludovice (1997) and Piacente (2005).

In 2006, biofuel production (ethanol) from sugar cane distillation started in five sugar cane factories (*ingenios*) located in Valle del Cauca (Colombia). Nowadays, around 11,000 ton $yr^{-1}$ of liquid vinasse (between 6-15 $m^3$ per ha) are applied as fertiliser (fertigation) for sugar cane to cover 42,000 ha where the valley-aquifer outcrops; vinasse application will cover more than 200,000 ha in the near future. This aquifer is the main water supply for more than 1 M inhabitants and 350 industries in the area, and provides agricultural irrigation for approximately 130,000 ha. Liquid vinasse for fertigation, a mixture of vinasse with urea (25% - 45% urea) with different commercial names (Vinurea®, Mayavin®, Provin®, among others) or solid (compost), is directly applied either manually to soil or through soil injection with specific devices fitted on lorries to avoid surface runoff. The legal framework includes no specific measures for implementing agricultural practices against the pollution of water resources or soil from vinasse. However, specific regulations have been developed for Valle del Cauca by the Corporación Autónoma Regional del Valle del Cauca-CVC local administration (Resolución 0100. No 06300081, 2012).

This study attempts to evaluate whether, and to what extent, the chemical characteristics and hydraulic properties of the unsaturated zone and aquifer are affected by vinasse application by taking into account hydrogeochemical and unsaturated zone aspects. In order to analyse the possible environmental impacts on the soil and aquifer in the study area, it was considered necessary to monitor the infiltrated vinasse in the unsaturated soil and aquifer in three fully instrumented experimental plots located in the Valle del Cauca (Cali, Colombia) sugar cane agricultural lands for the 2006-2011 period. The study constitutes only one aspect of a more comprehensive programme for the assessment of vinasse impacts by agricultural use and any possible long-term environmental risks. This work will also improve understanding of vinasse contribution to flow and transport processes to groundwater and unsaturated zones in a tropical climate.

## 2. Study area

Valle del Cauca (Colombia) is an alluvial plain located to the South of the corridor that runs between Barranquilla (NE) and Cali (SW) (Fig. 1). The study area is located in the southern part of the Valle del Cauca River Basin in Cali, which is an intermountain-savannah area plain, is characterised by a smooth relief and with a mean ground surface elevation of 1200 m.a.s.l. The main permanent surface water is the Cauca River. Valle del Cauca has a typical tropical climate with an average annual temperature of 24ºC and annual precipitation of 1,400 mm. One important aspect of the precipitation pattern is a tendency for heavy rainfall during short periods of time on an irregular basis due to a tropical climate, as well as the El Niño and La Niña events. The occurrence of La Niña 2010-2011 event has been considered to be the strongest episode since 1949 which brought about torrential rain. At the study site, an increase of precipitation of 36% and 17% with regard to the average year was observed for 2010 and 2011 respectively . The heaviest rainfall took place during the last quarter of the year with an increase of 86% and 19% for 2010 and 2011 respectively.

Land-use mainly consists of urban developments and cultivated crops. Agriculture is the primary land use of the area for sugar cane cultivation; other common crops include coffee, garden vegetables, bananas, maize and other fruits. Within the agricultural area, 360,000 ha are under irrigated management; irrigation water is pumped directly from the Cauca River diversion canals or from wells in the field. Groundwater is the main water resource in Valle del Cauca, and covers industrial and urban water supply demand and irrigation needs as there is no permanent surface water to rely on for water drinking supply.

From a geologic standpoint, Valle del Cauca (Fig.1) is a NE-SW trending graben basin of 6,900 $km^2$, and is filled with post-orogenic Quaternary materials (silt, gravel, limestone and conglomerates). It forms part of the folded, faulted and thrusted Andes belt (western and central mountain ranges) made up of Mesozoic and Cenozoic of volcanic and sedimentary materials with a maximum height of 4,100 m. The sediments from the Quaternary age that fill the intermountain plain are a fluvio-sedimentary formation of the Cauca River (CVC, 2012a). The Quaternary may be more than 1,000 m deep, and is composed of sand and silt with discrete gravel deposits in a channelled pattern as a result of the fluvial process. The bedrock is composed of impervious volcanic formations of Cretaceous age. However locally, structures of an older age may appear. Soil types are classified as vertisols and mollisols according to the USDA soil taxonomy.

The experimental plots are located in the Cauca River valley (Fig. 1), and in the sugar cane farming fields (known locally as *Haciendas*-Had. or *ingenios*) named Real, Santa Lucia and Zainera.

## 2.1. Hydrogeological setting

The lower Cauca study area forms part of a larger quaternary hydrogeological area that extends along the Cauca River. Detrital aquifers have developed mainly in quaternary materials, and are generally unconfined, although changes in facies and geological structures may impose local confined or semi-confined conditions. In the area of interest where research is being conducted and described in detail by Medina and Páez (2001), quaternary aquifer thickness is above 600 m. Two aquifers (upper and lower), separated by a clay layer, have been defined (CVC, 2012a). The aquifer considered herein is the upper one or 'A unit', with an average thickness of 120 m, and is an important unconfined detrital aquifer with some confined areas (Fig. 2). It is composed by heterogeneous layers of sand and gravel with interlayered silt and clay. Groundwater reserves can be estimated at 10,000 $Mm^3$.

Hydrologic data provided in the CVC (2012b) report for water table elevation contour maps indicate that the groundwater flow direction is E-W to the Cauca River, with a gently hydraulic gradient in the study area. Groundwater depth is around 1-2 m below ground level in the lower part of the plain and typically greater that 10 m in upland areas, with seasonal water level variations up to 4 m. The transmissivity values range between 150 and 2,200 $m^2\ d^{-1}$. Recharge sources come from precipitation (270 $Mm^3\ yr^{-1}$, average year), stream water, irrigation returns, wastewater, and domestic/industrial supply losses. Aquifer discharge is from irrigation, water supply, livestock, springs and additionally lateral flows to the Cauca River. Around 90% of groundwater demand is used in agriculture for sugar cane irrigation. According to the local Water Authority (CVC, 2012a), the aquifer is in equilibrium as regards water balance.

Groundwater chemical background signature (Table 1, 2004 data) presents low mineralisation a calcium/magnesium-bicarbonate facies, with a neutral pH (~7) and low electric conductivity (EC) values (500-1,100 $\mu S\ cm^{-1}$). Groundwater pollution is no great concern; nitrate contamination from agricultural sources only occurs at very specific local level mainly due to the use of nitrogen fertilisers; industries and sanitary landfills do not constitute a threat to groundwater resources.

## 3. Methods

A detailed characterisation of the vadose zone and groundwater was obtained during the study period in three experimental plots (Had. Real-R, Had. Zainera-Z and Had. Santa Lucia-S, Fig. 1). For the unsaturated zone only data for the 2008-2011 period are discussed.

In each plot four different subplots were defined and the following vinasse dose was manually applied ($K_2O$ per ha was the indicator used; Fig. 1): no treatment, 90, 180 and 270 kg of $K_2O$

ha$^{-1}$. Potassium is an essential sugar cane nutrient and is removed from the soil by plants; it also presents a narrow range of concentration in natural waters due generally to the preferential incorporation into clay mineral structures. These amounts are mixed with 46% of urea as N source, and were applied in a solution of 1.9-6.8 m$^3$ of vinasse per ha. For the quality impact assessment in the vadose zone and aquifer due to vinasse application, changes of $K^+$ concentration in water was monitored over time. Water samples were collected using standard sampling techniques, sampling bottles were filled to the top and ice-chilled stored until analysed.

Daily meteorological data, including precipitation, average temperature, hours of sunshine, humidity and wind velocity, were compiled from the weather stations located in the area and provided by the Centro de Investigación de la Caña de Azucar (CENICAÑA) meteorological network. Data on the amount of applied irrigation (several campaigns, depending on precipitation and sugar cane requirements) and vinasse composition were provided by the *haciendas* and the CVC. For the considered period (2008-2011), precipitation accounted for 1123 mm yr$^{-1}$, while average irrigation dose was 3564 m$^3$ ha$^{-1}$ yr$^{-1}$).

A summary of the activities (irrigation, vinasse applied) that were undertaken in the area is presented in Table 2. Plots management was jointly controlled by the Environmental Department in charge of the experimental research programme on the sugar cane cultivation of each *ingenio* and the CVC.

Instrumentation for the vadose zone and groundwater monitoring was installed prior monitored period. The plot designs, field measurements and samples collection and laboratory work carried out are provided in detail below.

### 3.1. Characterisation and monitoring the unsaturated zone

Three experimental plots (Fig. 1) located in the study area and covering cultivated surfaces that ranged between 4.7 and 6.8 ha were selected to assess water recharge and water quality changes through field research (Table 2). Each experimental plot had a piezometer, suction cup lysimeters and tensiometers (Fig. 3). Monitoring focused on the hydrodynamics of water infiltration, and also on chemical aspects based on available data set for this time period.

The upward-downward flux of water in the unsaturated zone was monitored weekly by tensiometers (Soilmoisture®); the tensiometer water reservoir was periodically refilled to maintain optimal conditions. Suction cup lysimeters for pore water sampling were maintained with a vacuum weekly. Suction cup lysimeters and tensiometers were vertically installed side by side by manual drilling at depths of 0.3, 0.6, and 0.9 m, with duplicates whenever possible; one suction lysimeter at 0.2 m was also included in the plots. To assess the water quality in the vadose zone, only $Ca^{2+}$, $K^{+}$ and $NO_3^{-}$ were the ions taken into account, plus EC. Sampling included an initial survey at the start of the project and two field campaigns (2010-2011). Soil texture and pore-liquid suction are properties that control the amount of liquid that can be removed by a porous cup sampler. Due to the hydraulics of the unsaturated zone, the volume of liquid collected at a given time did not suffice for comprehensive laboratory analyses, limiting the number of chemical parameters determinations for water samples.

Triplicate undisturbed soil samples were collected at depths of 0, 0.10, 0.30 and 0.9 m by manual drilling after vinasse applications. They were hermetically sealed to be transported to the laboratory to determine their physical and chemical soil properties (texture, bulk density, grain size distribution, water content, porosity) following ASTM standards. For the soil-water characteristic curve (suction curve) determination, undisturbed soil samples were also taken at depths of 0.1-0.20, 0.20-0.30, 0.30-0.60 and 0.60-0.90 m from an excavated trench, and the pressure cell method was applied. All the soil parameters were determined in the CIAT laboratory (Palmira, Colombia). Soil chemical composition and soil mineralogy were obtained through XR analysis (Jones, 1991) at the CSIC-Jaume Almera Institut (Barcelona, Spain).

Unsaturated hydraulic conductivity was obtained at CIAT from the soil water retention curve (SWRC) of the observed soil water retention data, which defines the relationship between soil water content and hydraulic potential. The RTC 6.02 code (van Genuchten et al., 1991), based on the van Genuchten-Mualem model (van Genuchten, 1980) which defines the relationships between soil-water content and hydraulic potential, was applied to estimate the van Genuchten parameters equation.

Thirty infiltration tests (with water and vinasse) were *in situ* run at the three field sites by the double-ring infiltration method following ASTM D3385-09 (2009). Experiment sites were selected according to their hydrogeological characteristics and for fulfilling test development requirements. Additionally, *in situ* hydraulic conductivity at depths of 30, 60 and 90 cm was also obtained according to the Guelph permeameter method (Salverda and Dane, 1993).

### 3.2. Aquifer monitoring

Water table elevation and quality were controlled throughout the experimental period through the CVC monitoring network, which consists of 30 piezometers for water level control and 15 piezometers for water sampling**.** During the experimental study period, groundwater was sampled at dry and rainy periods from the wells and piezometers located in each experimental plot following vinasse application. Groundwater monitoring included previous campaigns (data base starts in 2006) before the experimental phase, to assess the aquifer baseline. The samples obtained from wells were either pumped or bailed, depending on whether or not the pump was working, while piezometer water samples were manually bailed. For all the water samples, temperature, EC and pH were determined *in situ*.

The major ion content, hardness, pH and electrical conductivity of the water samples were analysed following standard procedures at the CVC laboratories. The assessment of the characteristics of major ions and groundwater quality was made by applying classical hydrochemical tools for characterising patterns, chemical processes and interactions (Appelo and Postma, 2006). The hydraulic conductivity of aquifer media was obtained by the pumping tests done by the CVC within the study framework.

## 4. Results and discussion

### 4.1. Unsaturated zone

From the lithological point of view, the vadose zone in the studied area is constituted by alluvial sediments of a silty-sand texture with interbedded clay layers and organic matter. Total thickness ranges between 0.95 and 3.30 m; soil pH is between 5.5 and 7. Main predominant minerals are quartz, plagioclase and amphibole; chlorite and illite are the clay minerals present.

For the Had. Real site (Fig. 1), a sandy loam texture characterises the first 1.6 m approximately, and vadose zone thickness was between 2 m and 3.30 m. In Had. Zainera, the soil profile was composed of silty loam layers with aggregates of carbonate particles of up to 2 m, approximately; vadose zone thickness was around 2.6 m. In Had. Santa Lucia, the soil profile texture was constituted by silty clay with organic matter and a carbonate crust, and the vadose zone ranged between 0.9 m and 1 m. In this last *hacienda,* clay lenses gave rise to a temporary perched water table in the vadose zone during heavy precipitation periods, which led to an intermittently saturated zone and anomalous tensiometer readings. Consequently, the recorded values were not taken into account for this study. Only the results from Had. Real and Zainera sites are discussed herein.

According to the permeameter field results, the average hydraulic conductivity for the first 90 cm of the soil profile was extremely heterogeneous, with average values ranging between $3x10^{-7}$ and $3x10^{-4}$ m $s^{-1}$ for the two haciendas, being slightly lower for Zainera. Values at the selected depths are shown in table 3. Although these values correspond to water content for test development and may not reflect real field hydrodynamic characteristics, they constitute an indicator of flow and transport conditions. The infiltration test results gave values ranging between $1.9x10^{-6}$ - $45.0x10^{-6}$ m $s^{-1}$ (for water) and $0.14x10^{-6}$ - $10x10^{-6}$ m $s^{-1}$ (vinasse application) for Had. Real, and $11.7x10^{-6}$ - $15.2x10^{-6}$ m $s^{-1}$ (water) and $0.28x10^{-6}$ - $18.1x10^{-6}$ m $s^{-1}$ (vinasse application) for Had. Zainera. Infiltration velocity was conditioned by the soil water content (greater with wet soil) and brix degree of the applied vinasse and soil profile composition. The increase in the brix degree, which implies more dissolved solids, slowed down infiltration velocity.

The water state (pressure head) in the vadose zone for both field sites (Real and Zainera) during the monitored period, along with precipitation and the irrigation application, are plotted in Fig. 4. The vadose zone water flux movement shows a similar behaviour pattern of the suction potential in both plots and soil depth, with groundwater recharge, or the water that passes through the vadose zone and enters the groundwater system, controlled mainly by the amount of water entering the ground surface by infiltration. Flow was dynamic and characterised by upward flow periods (more negative suction values) and episodes of downward flow (less negative), mainly in response to hydrologic events.

The Had. Real readings, taken at different depths, showed less fluctuation, which may be the result of more homogeneous soil media and of a sandy composition which favours low suction variability. The tensiometer placed at the 90 cm depth had to be ruled out after a short monitoring period for technical reasons. In the Zainera plot, the effect of the amount of precipitation from the ‘La Niña’ (2010-2011) saturated the vadose zone surface layers of silty loam composition. The strong La Niña event also contributed to the record flood events seen during this period. This was observed given the temporal saturation of the tensiometers placed at the 30 cm and 60 cm depths (suction potential readings came close to 0 cm), and also given the observed permanent readings taken by the tensiometer placed at 90 cm, which indicated soil saturation at this depth. Nevertheless, it is important to note that lateral flow may also contribute to this effect.

Downward flow estimations made during rainy periods may reach up to 1 m day$^{-1}$ similar to the highest values provided by infiltration tests. It was possible to observe these effects from the increasing groundwater level trend after the 2010 and 2011 rainy seasons. The flood events increased soil profile saturation while decreasing water tension and enhancing infiltration. From the theoretical point of view, it is well-known that a more rapid response of infiltrating water is produced after rain in moist soil. As hydraulic conductivity depends on soil-water tension, soil with higher water content displays greater hydraulic conductivity and a poorer water storage capacity for infiltrating water, which causes the water front to advance more rapidly.

According to the chemical composition (2010-2011 period, available data records), pore water in the vadose zone belonged to the carbonate calcium-magnesium facies, and presented a higher mineralisation than that observed in the aquifer. Baseline information prior to vinasse application does not exist.

### 4.2. Groundwater

For the research period, the groundwater depth was between 1 m and 4 m below the ground level in the experimental plots, with the lowest groundwater depth recorded for Had. Real. As shown in Fig. 5, the groundwater level change responded well to water input with a time lag of a few weeks. Groundwater dynamics was seen to be highly conditioned by one of the most severe precipitation rates reported in the zone during the La Niña 2010 period, which had a direct effect on aquifer recharge, as clearly observed by the Had. Zainera groundwater level, with an increase in the water table of up to 3.5 m from May 2010. Groundwater fluctuation for the monitored period was around 2 m. Differences of groundwater level is likely due to varying geologic subsurface infiltration characteristics and discharge pathways.

Aquifer hydraulic conductivity from the pumping tests gave values of 20 m $d^{-1}$, with 6 m $d^{-1}$ for Had. Santa Lucía. The major presence of clay lenses in aquifer media, also observed in the vadose zone characterisation, resulted in this low value. Porosity values ranged between 32% and 41%, and flow velocity was estimated to lie between 50 and 60 cm $d^{-1}$, considered to be average for this type of aquifer materials.

The water quality values prior to vinasse application (average data provided by the CVC) are shown in Table 1. The hydrochemical data from the 2004 sampling campaign show that groundwater was composed of calcium-magnesium bicarbonate facies and presented low mineralisation, with EC values ranging between 20-1120 μS $cm^{-1}$, and hardness between 380-564 mg $CaCO^3$ $L^{-1}$ of. All the pHs were neutral.

## 4.3. Effect of vinasse application on unsaturated and saturated zones

For the unsaturated zone, the water chemical results from the suction cups (the 2010 and 2011 campaigns, with limited analytical data in both experimental sites, Real and Zainera), indicated a sharp drop in the concentration of major ions compared to the applied vinasse dose. The EC measured values, as a representative parameter of dissolved solutes in water, ranged between 295-547 (2010) and 150-1,269 (2011) μS $cm^{-1}$, significantly lower than reported values, between 4,000 and 64,000 μS $cm^{-1}$for the applied vinasse (Table 1). For the available chemical analysis records the following concentrations were found (CVC, 2012a): 8-29.7 mg $SO_4^{-2}$ $L^{-1}$; 1.51-7.61 mg $NO_3^-$ $L^{-1}$ and 2.9-6 mg $K^+$ $L^{-1}$. Generally, the highest concentration was always detected at 90 cm deep, except for the $K^+$ with the opposite behaviour, maybe related to sugarcane uptake, evapotranspiration process together with the maximum development of sugar cane roots at around 60 cm (85% roots density). Solid organic compounds in sugarcane residues added to soils also provides new exchange sites for cations as well as other adsorption sites (Rosabal et al., 2007). Nevertheless, it needs to be notice that due to data scarcity these results must be considered as an indicator of the system performance. When considering the chemical characteristics and concentration of the applied vinasse (Table 1), the concentration of chemical compounds (major ions) drastically lowered after entering the unsaturated zone influenced by subsurface hydrologic processes (sorption, precipitation, transformation, biotransformation, etc.; Appelo and Postma (2006)), taking place in the soil profile, together with sugar cane uptake, fact also observed by other authors (Gloeden et al., 1991). The results found in the literature show that accumulation of nutrients in plant (leaves, stalks, roots) may reach 271 kg N $ha^{-1}$, 99 kg P $ha^{-1}$, 149 kg K $ha^{-1}$, 112 kg Ca $ha^{-1}$, 71 kg Mg $ha^{-1}$and 71 kg S $ha^{-1}$ (Rengel et al., 2011); no data have been found for other nutrients. For the Cauca Valley, values of 250 kg K $ha^{-1}$ in sugar cane have been found according to CENICAÑA data. The ion oxides concentration in the vadose soil profile provided by RX analysis presented no changes over time; according to the obtained results salinization in the soil profile is not observed as bulk storage increase in $O_2Na$ or $O_2K$ did not took place.

During the study period, the groundwater composition of the monitored wells located in the experimental plots showed an increase in dissolved ions and EC by infiltration of enriched recharge waters to water table. This is likewise observed in the works of Hassuda (1989), Ludovice (1997) and Piacente (2005). An indication of water quality variation based on some hydrochemical values reported from 10 selected wells has been plotted for the May-June sampling campaigns in both 2006 and 2012 (see Fig. 6 and complementary material). All chemical analyses displayed an acceptable difference in the cation-anion balance. For the sake of simplicity, only the most interesting parameters as regards changes are shown. Similar to 2006 chemical signature, for the 2012 samples the $HCO_3^-$ is the dominant anion, no changes in pH were observed. All the ions showed an increasing concentration trend in groundwater; the most significant enrichment corresponds to $Ca^{2+}$, $Mg^{2+}$ (also supported by the hardness graph of Fig. 6c) and $K^+$, with an increase rate of more than 50% independently of the dose applied. The wells reflect the impact of the different vinasse application doses (0, 90, 180, 270 kg of $K_2O$ per ha) on groundwater, but also contribution of local flux to water chemistry is expected as observed at sampling point R (0 and 0’), which is representative of groundwater in a plot with no vinasse application.

For 2006 and 2012, the major chemical elements of the 10 selected wells of the three plots were plotted in the Piper diagram (Fig. 7) which indicates composition of water expressed by total ions, existence of linear trends or other relationships that can be geochemically interpreted; average vinasse value of chemical concentration is also represented for comparison purposes. The figure shows that according to water chemistry there is only one group of aquifer water type of calcium-magnesium bicarbonate composition. The temporal evolution of groundwater chemistry in the sampled wells between the 2006 (with chemical signature originated before vinasse application) and 2012 sampling campaigns denoted a linear behaviour, clearly observed by changes in the cations field. There are no detectable changes in the anions field ($CO_3^{2-}$+ $HCO_3^-$, $SO_4^{2-}$). Slight increase in $Ca^{2+}$ and $Mg^{2+}$ decrease was observed in some well samples (see also Fig. 6d) the contribution of $Na^+$ and $K^+$, but mainly increase of $Na^+$; $K^+$ exhibits strong tendency to be reincorporated in clay minerals, like in Mauritius soils (Soobadar and Ng Kee Kwong, 2012). The minor change is produced in well R (0 and 0'), and cationic exchange is suggested to occur in all sampled waters except for Santa Lucia wells, flooded by the heavy rainfalls during some periods.

The relative ions concentration and distribution encountered in the different sampled wells is related to: aquifer geologic heterogeneity (variations due to existing lithological facies); the importance of local recharge, specially by La Niña event, compared to the regional base flow; the applied vinasse dose; and the experimental plots location and subsurface processes taking place. The observed variation did not apparently indicate a direct relationship with the amount applied. However, the fact that extensive temporal data sets were lacking did not allow us to be conclusive although we believe are representative for the monitored period. The small ions variability in groundwater samples, apart from the errors derived from analytical issues and derived calculations implies and added difficulty for and adequate process understanding.

## 5. Conclusions

The results obtained during the monitored period in the study area showed slight groundwater quality changes in terms of increased dissolved salts, being controlled by geochemical processes and plant growth. After six years of vinasse application, the 2012 groundwater samples clearly indicate mixing of the fresher groundwater with the applied vinasse. Enrichment of ions in groundwater, especially for $Na^+$ and $K^+$, was probably due to the cationic exchange linked to decreasing $Mg^{2+}$ during transport in the unsaturated zone; calcite dissolution may have also contributed to the increase in $Ca^{2+}$ and $Mg^{2+}$ over time. Yet on the whole, all the water in the three experimental plots presented a very low major ion concentration, and the chemical composition of water was of good quality. It is also worth mentioning the strong La Niña effect on aquifer recharge which would dilute the infiltrated water during the monitoring period and, on the other hand dissolution of possible precipitated salts bringing them back into solution may occur. The rather narrow range of ions concentration observed in groundwater suggests a significant control mechanisms may be involved. The hydrochemical variability observed in the various sampled wells was a response to the spatial heterogeneity of the aquifer media, and to temporal mixing and dilution with applied vinasse, irrigation water and meteoric recharge. Most vulnerable experimental areas appeared to be Had. Real, because of sandy composition, this favoured water infiltration and leaching.

For the monitored period, vadose zone salt or ion oxides storage were not observed in the soil media, probably associated with removal by sugar cane, and with the high rainfall hydrologic conditions in the study area. Similar vadose zone water behaviour was observed in Had. Real and Zainera, while Had. Santa Lucia showed a temporary perched water table, produced during heavy precipitation periods due to the clay composition of soil media. Subsurface hydrologic processes occurring in soil profile lowered concentration of chemical compounds. Compounds that enter the vadose zone will tend to move more slowly than in the saturated zone because of the processes taking place in this part of the aquifer (matric and osmotic potentials are significant forces that affect water movement), which slows down the water movement rate. The unsaturated zone, acted as a system for groundwater contamination prevention and for downward flow estimation, which implies aquifer recharge and contaminant transport. The nutrients uptake by sugar cane in the upper 60 cm of soil profile as part of the soil transport process needs also to be highlighted.

Given the complexity of water-soil-plant systems and the space-time variability of the processes involved, in order to determine the risk of groundwater pollution that results from specific land management practices, detailed research to better capture vinasse transport through the unsaturated zone by means of mass balance is necessary. Also, investigation of consequences derived from different hydrologic conditions (more pronounced dry periods) and influence of pH changes and DOC on metal leaching needs to be addressed. As vadose zone hydrochemical background is difficult to establish, baseline data acquisition (measured at a point at time) can provide the needed information for establishing post-vinasse application impacts. The use of numerical models to represent the observed hydrological and transport response as a decision tool to predict the effects of alternative management strategies on water quality is a necessary second step to be considered.

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## Supplementary data

Supplementary data include water chemical composition and corresponding Piper diagram of selected wells described in this paper and a google map of the area.

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**Figures and table captions**

Fig. 1. Study area, geological setting and location of experimental plots. A detailed sketch of applied $K_2O$ dose in plots is also shown.

Fig. 2. The Cauca river aquifer system sketch.

Fig. 3. Layout of the experimental plots instrumentation

Fig. 4. Vadose zone pressure head *vs*. precipitation plus irrigation for experimental plots Had. Real and Zainera. Since August 2009, no data has been available at the depth of 90 cm for Had. Real due to a technical failure. Notice that for Zainera data records start in May 2009.

Fig. 5. Groundwater level change *vs.* precipitation and irrigation throughout the monitoring period a) Had. Real (R0 well); b) Had. Zainera (Z3 well), c) Had. Santa Lucia (S3 well).

Fig. 6. Groundwater chemical values of a) EC ($\mu S\ cm^{-1}$), b) hardness ($mg\ L^{-1}$) c) $K^+$ ($mg\ L^{-1}$) and d) $Mg^{2+}/Ca^{2+}$ ratio for the selected monitoring wells located in the three haciendas (R: Had. Real; S: Had. Santa Lucia; Z: Had. Zainera). The black bar represents the concentration value of the parameter for a specific well during the 2006 sampling campaign, while the grey one denotes the 2012 data. The 1, 2 and 3 denotes application of 90, 180 and 270 kg of $K_2O\ ha^{-1}$ in the plot.

Fig. 7. Observed hydrochemical changes in selected monitoring wells (see Fig 4 and complementary material). The arrow indicates the change in samples concentration for 2006 and 2012 in the selected well. The ‘ denotes 2012 data for the same well. (R: Had. Real; S: Had. Santa Lucia; Z: Had. Zainera).

Table 1. Vinasse composition. Maximum, minimum and average concentrations (CVC, 2012a and 2012b).

Table 2. Experimental plots and activities done during the 2006-2011 period.

Table 3. Hydraulic conductivity distribution at selected depths. Permeameter field test results

Table-1

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| Parameter | Min-Max | Mean | Groundwater (2004) |
|---|---|---|---|
| pH | 3.98-5.1 | 4.7 | 6.8-7.6 |
| EC (μS $cm^{-1}$) | 4,350-64,099 | 32,803 | 543-1,120 |
| TDS (mg $L^{-1}$) | 117,416-599,400 | 358,578 | 458-702 |
| QOD (mg O $L^{-1}$) | 170,757-60,1832 | 35,0811 | 2.4-3.4 |
| Hardness (mg $CaCO_3$ $L^{-1}$) | 7,498-50,667 | 22,469 | 380-564 |
| $HCO_3^-$ (mg $CaCO_3$ $L^{-1}$) | 1,098-23,302 | 8,875 | 312-620 |
| $SO_4^{2-}$ (mg $L^{-1}$) | 8,901-35,670 | 21,276 | 25.4-124 |
| $Cl^-$ (mg $L^{-1}$) | 271-13,980 | 7,041 | 7.1-21 |
| $NO_3^-$ (mg $L^{-1}$) | 39-10,247 | 2,971 | 6-1.7 |
| $PO_4^-$ (mg $L^{-1}$) | 8.7-297 | 167 | 0.0-0.1 |
| $Na^+$ (mg $L^{-1}$) | 90.7-1,671 | 942 | 10.7-26 |
| $K^+$ (mg $L^{-1}$) | 4,698-46,950 | 19,515 | 0.8-1.6 |
| $Ca^{2+}$ (mg $L^{-1}$) | 879-10,133 | 4,316 | 45-114 |
| $Mg^{2+}$ (mg $L^{-1}$) | 1,272-6,080 | 2,818 | 34-89 |
| Fe (mg $L^{-1}$) | 0.5-21,125 | 4,286 | <0.2 |
| Cr (mg $L^{-1}$) | 50.6 | - | - |
| Ni (mg $L^{-1}$) | 3.8 | - | - |
| Mn (mg $L^{-1}$) | 23-6,410 | 2,146 | - |
| Phenol (mg $L^{-1}$) | 0.0-4.8 | 2.6 | <0.01 |

(CVC, 2012a,b)

**Table-2**

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| | | Real (4.7 ha) | | | | | | Zainera (6.8 ha) | | | | | | Santa Lucia (4.6 ha) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Year | | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 |
| Rainfall (mm) | | | | 918 | 681 | 784 | 1,049 | 817 | 1,461 | 1,619 | 756 | 1,002 | 1,400 | | 679 | 1,554 | 1,158 | 963 | 1,598 |
| Irrigation ($m^3$ $ha^{-1}$) | | 4,735 | 7,566 | 5,294 | 7,280 | 5,311 | 2,837 | 2,000 | 2,400 | 1,200 | 3,000 | 2,500 | 3,000 | 4,965 | 5,420 | 3,783 | 2,311 | 3,823 | 2,439 |
| Vinasse applied ($m^3$ $ha^{-1}$) | 90 kg $K_2O^*$ | | | 2.36 | 2.36 | 2.36 | 2.36 | | | 2.00 | 1.62 | 2.89 | 3.18 | | 1.9 | 2.1 | 1.74 | NA | NA |
| | 180 kg $K_2O^*$ | | | 4.67 | 4.67 | 4.67 | 4.67 | | | 4.00 | 3.24 | 5.76 | 6.36 | | 3.62 | 3.99 | 3.47 | NA | NA |
| | 270 kg $K_2O^*$ | | | 6.89 | 6.89 | 6.98 | 6.98 | | | 6.00 | 4.87 | 8.67 | 9.54 | | 5.84 | 6.45 | 5.03 | NA | NA |

$^*$ $ha^{-1}$ $year^{-1}$ , NA : Not available

**Table-3**

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| | Depth (cm) | | |
|---|---|---|---|
| | 30 | 60 | 90 |
| Had. Real ($m\ s^{-1}$) | $1.5x10^{-6}$ | $3.7x10^{-6}$ | $5.5x10^{-7}$ |
| Had. Zainera ($m\ s^{-1}$) | $58.3x10^{-7}$ | $1.2x10^{-5}$ | $2.2x10^{-5}$ |

Figure-1
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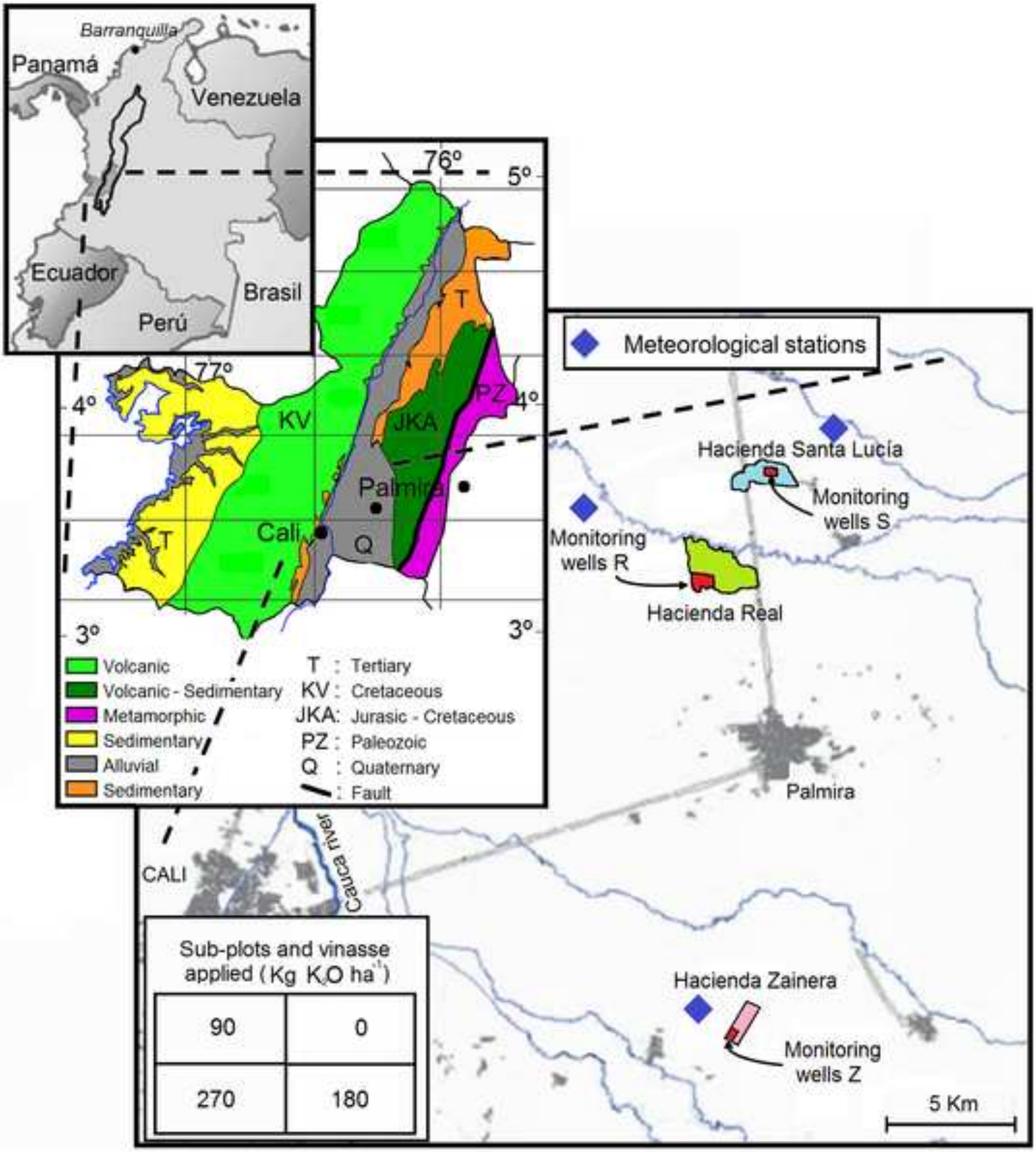

Figure-2
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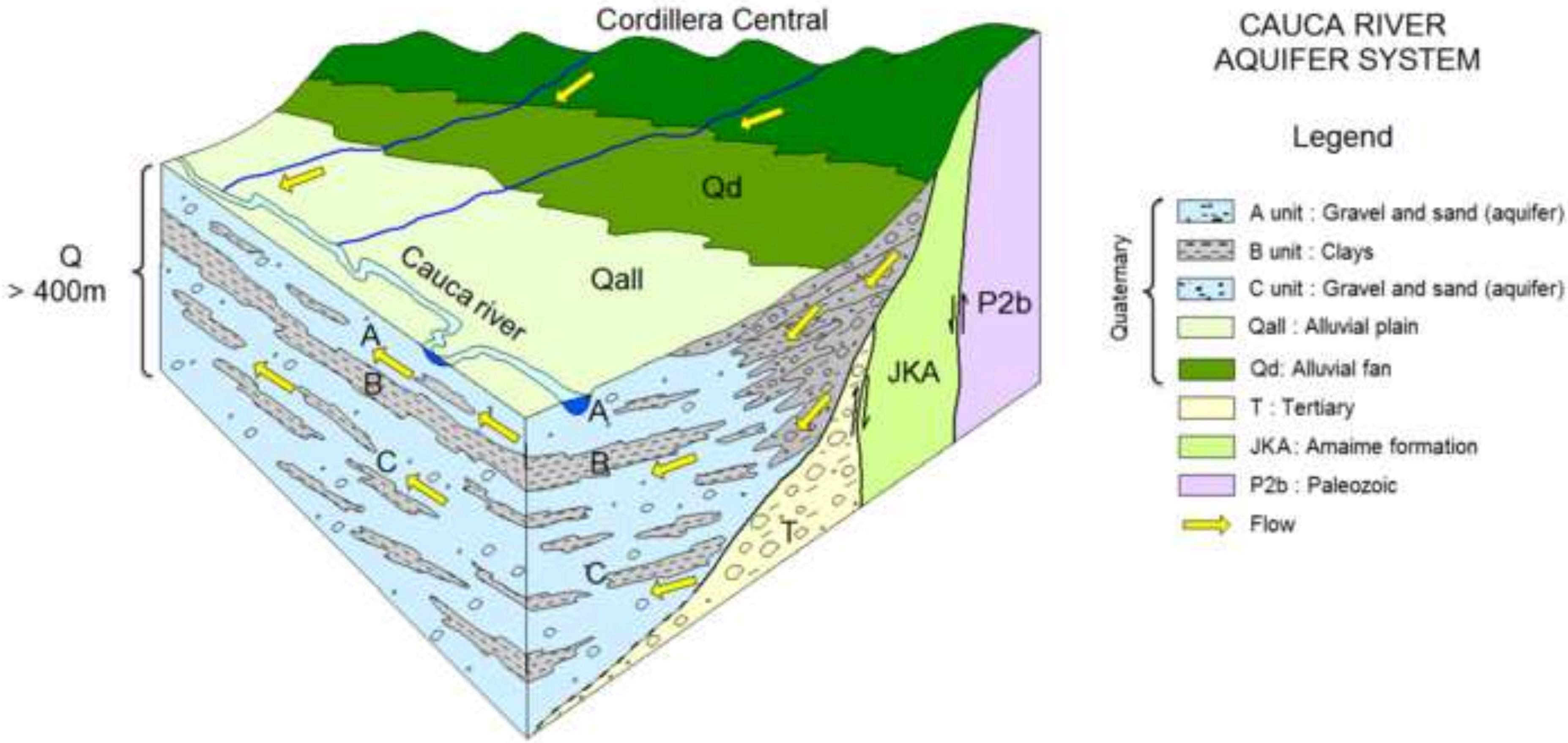

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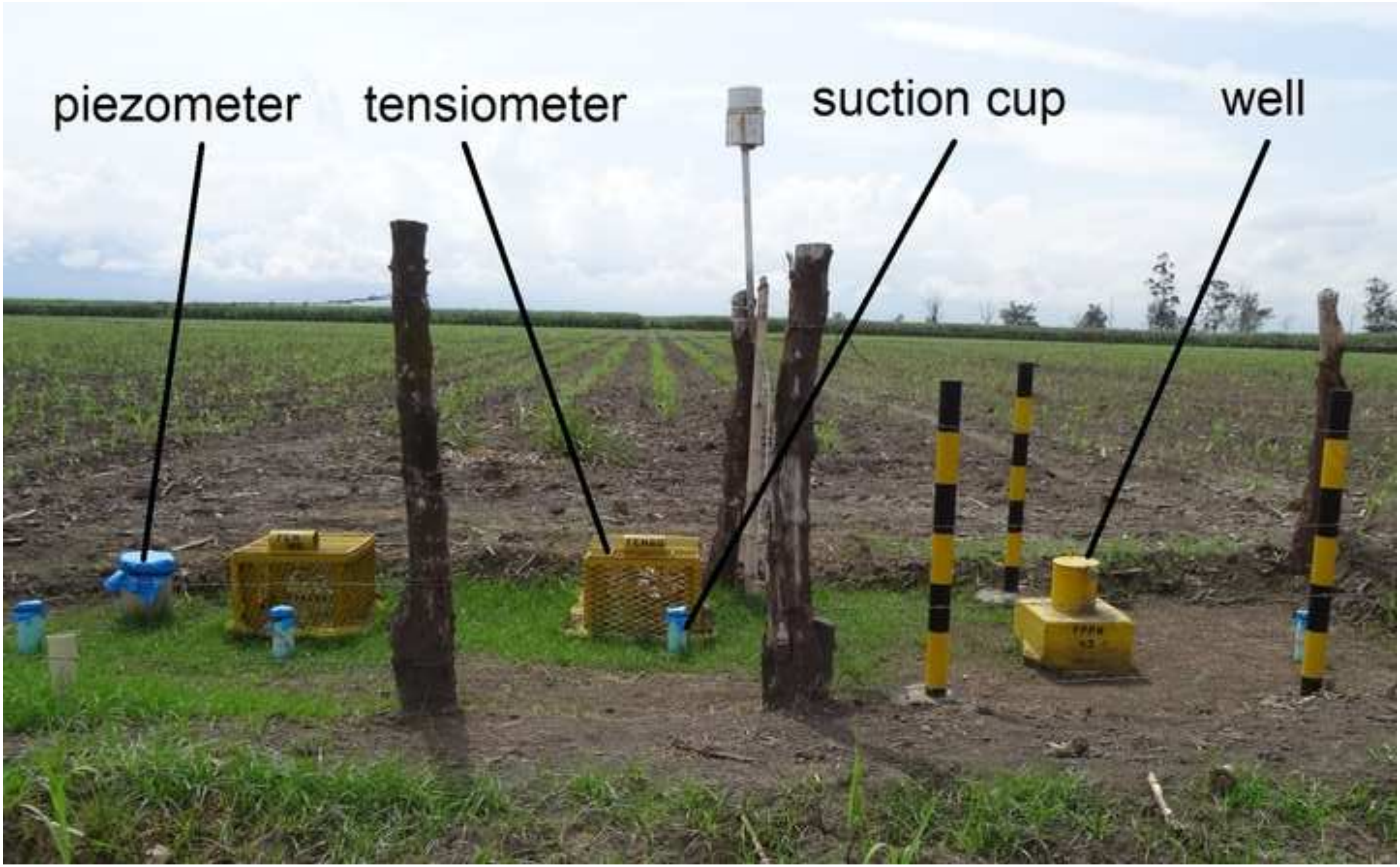

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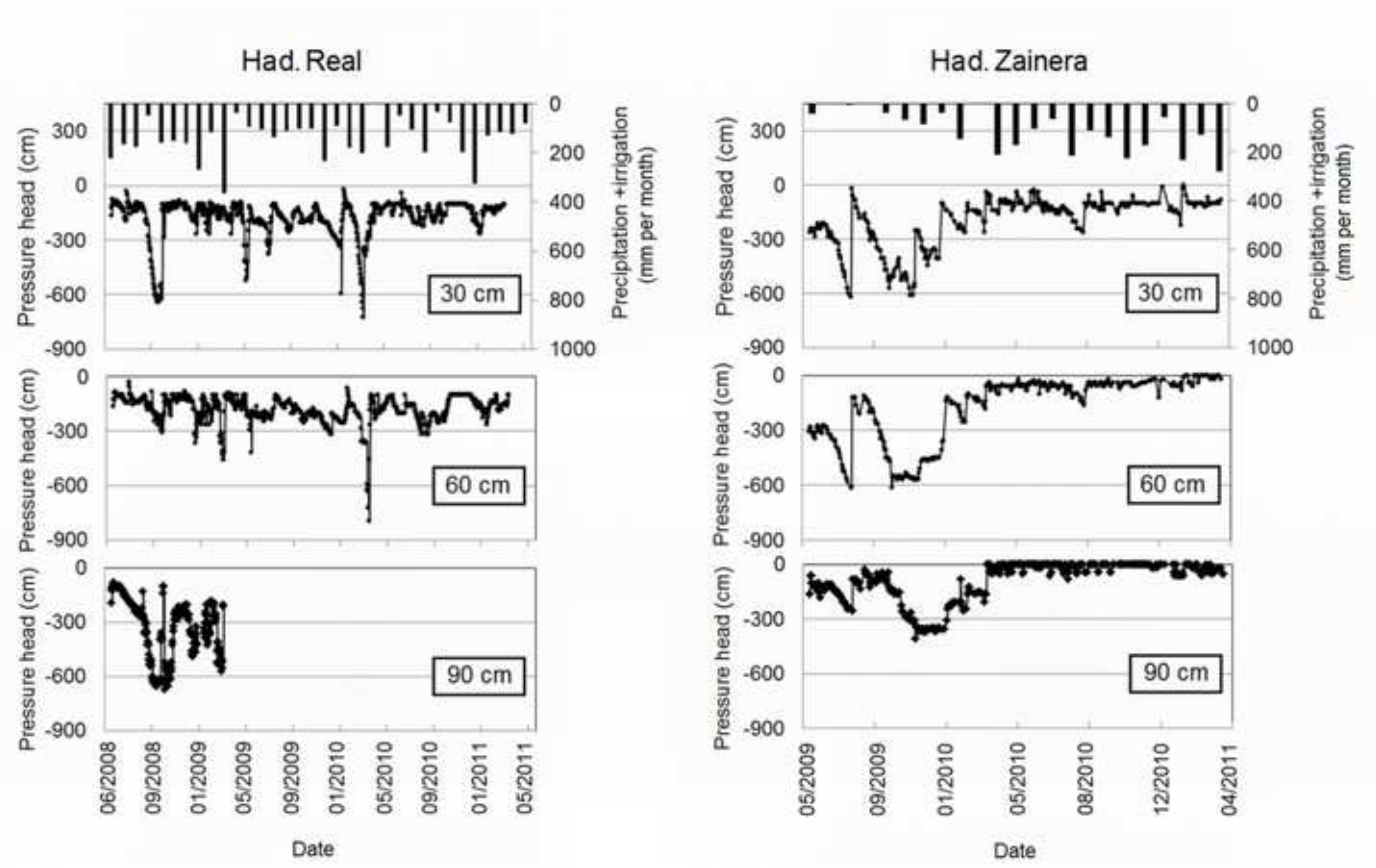

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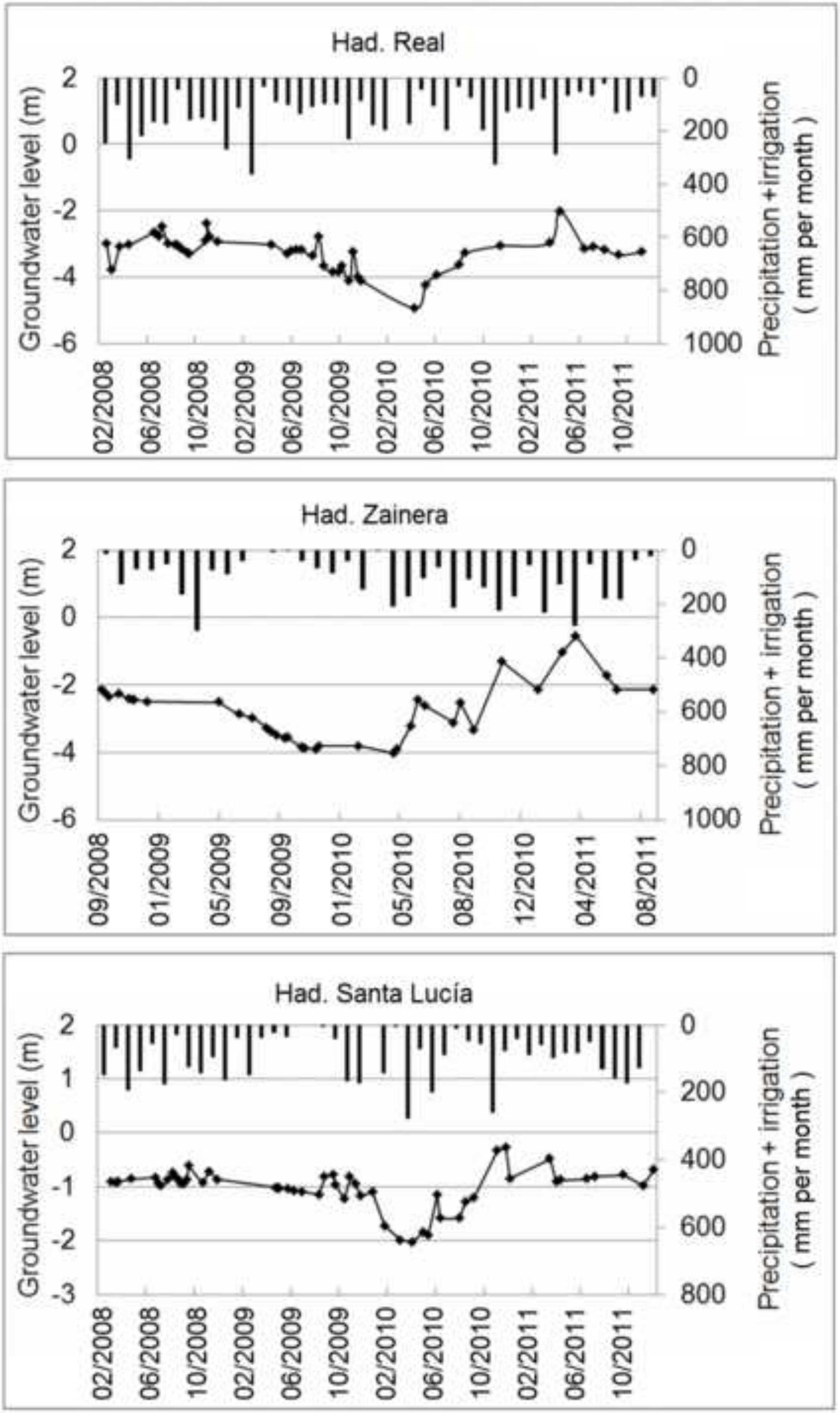

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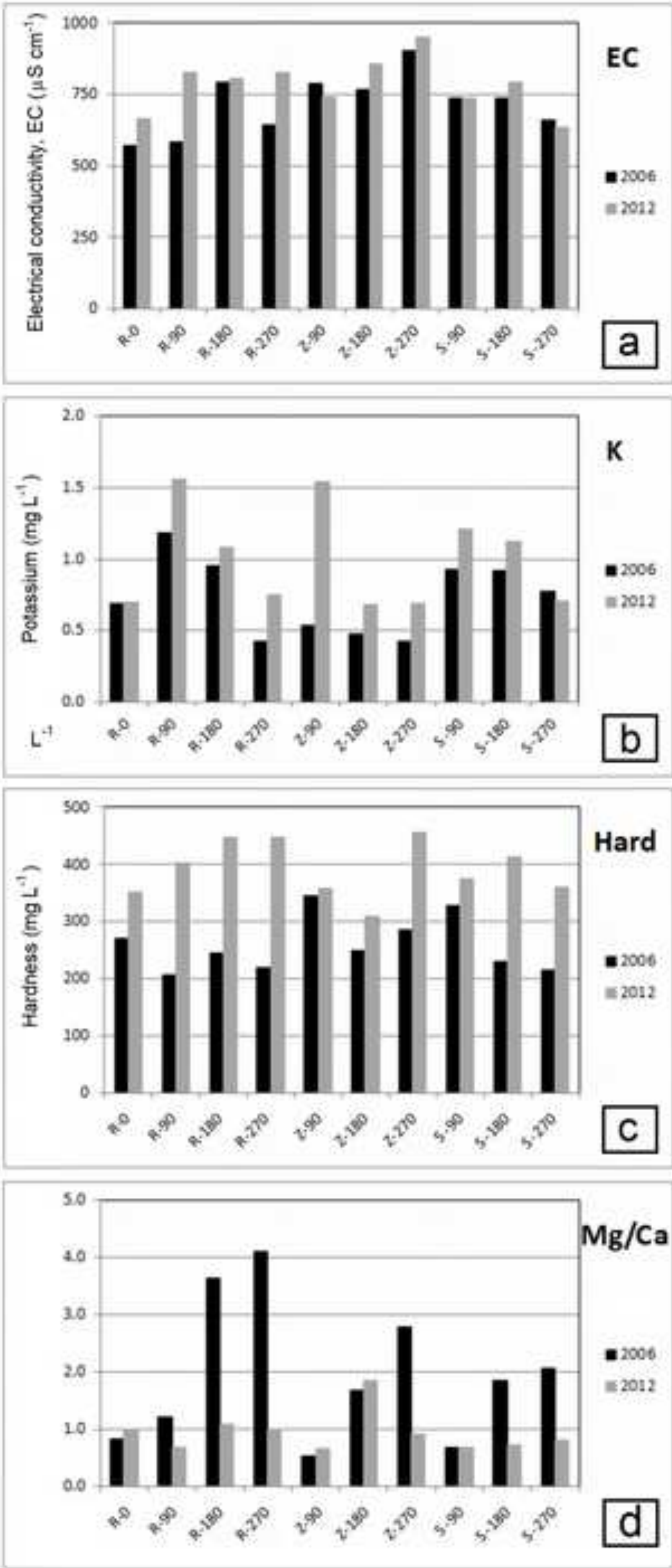

Figure-7

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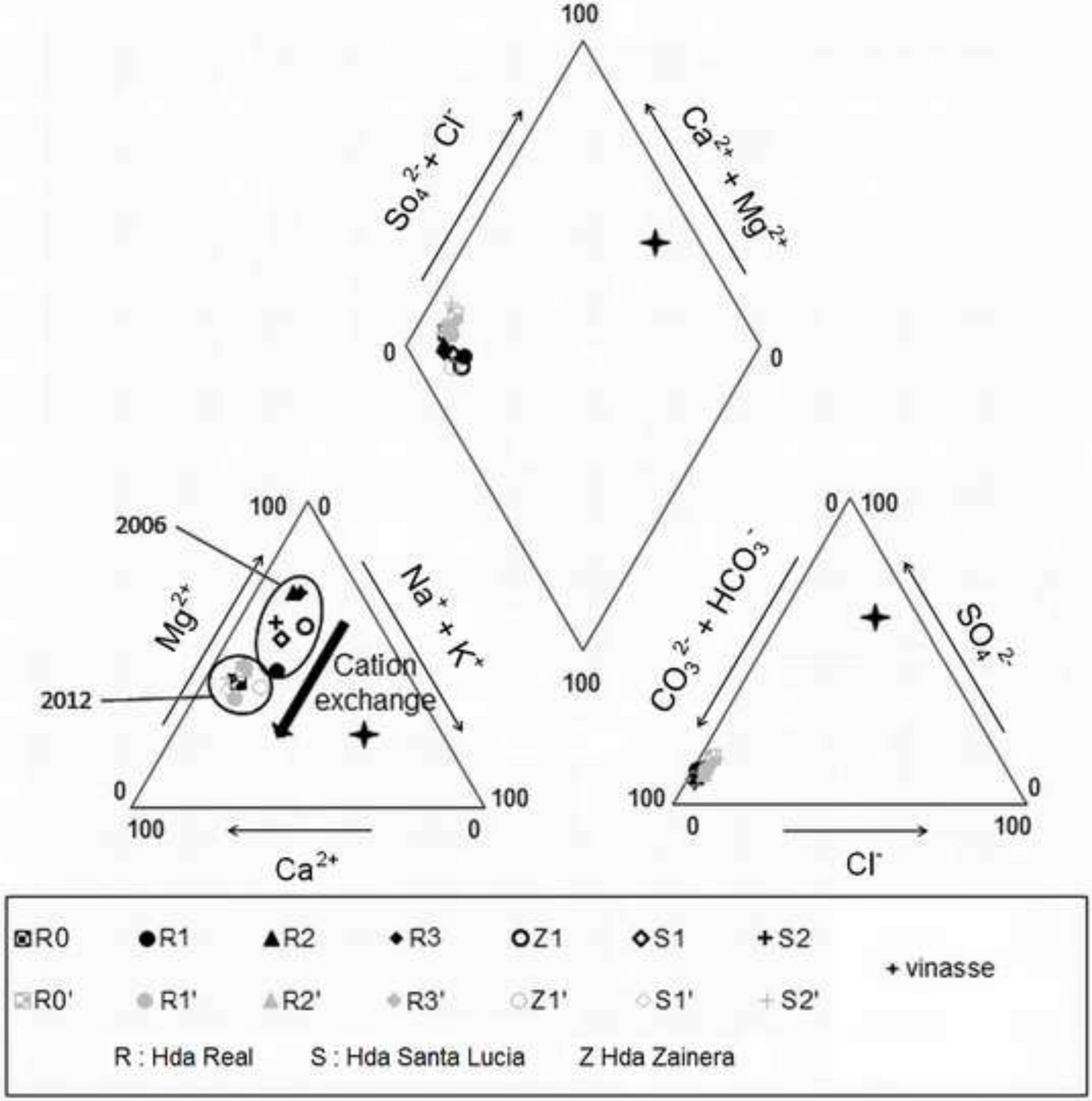

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Chemical analysis of selected wells

Piperdiagram of selected wells

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